

TENTATIVE IDENTIFICATION OF U93.174 AS THE MOLECULAR ION N_2H^+

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ABSTRACT

On the basis of a self-consistent field calculation of its rotation constant and hyperfine structure, it is suggested that the molecular ion N_2H^+ is the carrier of the unidentified interstellar triplet reported by Turner in the preceding *Letter*. The calculated frequency of the $J = 1 \rightarrow 0$ transition of N_2H^+ is 92.2 ± 1.8 GHz, in good agreement with the observed 93.1 GHz. Similarly, the calculated value of the quadrupole coupling constant for the outer nitrogen is -5.3 ± 0.5 MHz, while the coupling constant deduced from the observations is -5.7 MHz. Equally important to the assignment, the quadrupole coupling for the inner nitrogen is calculated to be only -1.2 ± 0.5 MHz, making its contribution to the hyperfine structure too small to be resolved in the sources so far observed. Detection of this additional structure in sources with very narrow lines would provide additional confirmation of the assignment.

Subject headings: molecules, interstellar — radio lines

Turner (1974) reported in the preceding *Letter* the discovery of three closely spaced new interstellar lines near 93.174 GHz. The structure of this triplet is characteristic of the hyperfine structure (hfs) produced by the electric quadrupole interaction of a single nitrogen nucleus in the $J = 1 \rightarrow 0$ rotational transition of a closed-shell molecule, and is in fact virtually identical to that of the nearby 88.6-GHz $J = 1 \rightarrow 0$ line of HCN. No molecule with a single nitrogen, however, has been found with the right spectroscopic constants to fit the observations.

The purpose of this *Letter* is to point out that the molecular ion N_2H^+ is an excellent candidate for the carrier of Turner's lines, although at first glance it might appear that the two nitrogen nuclei would give rise to more structure than observed. Simply by taking the bond lengths and hyperfine constants to be equal to those of similar molecules, one finds that the rotation constant and the hfs of the outer nitrogen are in substantial agreement with Turner's observations, whereas the hfs from the inner nitrogen is too small to have been resolved in the sources examined. These conclusions have been confirmed by an ab initio calculation of the structure of N_2H^+ , putting the identification on a somewhat more secure quantitative foundation.

N_2H^+ is isoelectronic with N_2 , CO, HCN, HNC, and HCO^+ , and its electronic ground state is expected to be an extremely stable closed-shell configuration. An estimate of its rotation constant can be made by assuming that the length of the NN bond is the same as in N_2^+ , about 1.11 Å, and that the length of the NH bond is about 1.00 Å. The result is $\nu_{10} = 2B = 92.2$ GHz for the lowest-frequency rotational transition—in reasonably good agreement with Turner's frequency. Furthermore, the hfs can be estimated by comparison with the isoelectronic isomers HCN and HNC. For HCN the

nitrogen hfs has been measured, and the coupling constant is $eqQ = -4.709$ MHz (DeLucia and Gordy 1969). Although eqQ has not been measured for HNC, an ab initio calculation (Pearson *et al.* 1973) predicts a coupling constant of only $+0.93$ MHz, with an estimated accuracy of better than 50 percent. Another estimate of the hfs for the outer and inner nitrogens can be obtained from measurements of CH_3CN and CH_3NC , which give $eqQ = -4.4$ MHz for the outer and $|eqQ| < 0.5$ MHz for the inner nitrogen (Townes and Schawlow 1955).

To check this reasoning we have done an ab initio calculation of the structure of N_2H^+ . The equilibrium geometry, the electric field gradients at the nuclei, and the permanent electric dipole moment have been calculated in the self-consistent field (SCF) approximation. The molecular wave function must be approximated by expansion in a finite basis set, and we have used Slater-type functions centered on the nuclei. It is easy to employ enough functions in a molecule as small as N_2H^+ to essentially reach the infinite-basis Hartree-Fock (HF) limit with current computational capability. Because the HF wave function is not exact, however, it is sometimes preferable to employ smaller basis sets and take advantage of the cancellation of errors known to occur when certain molecular parameters are calculated. The most accurate calculations of molecular geometry, for example, are obtained from a double-zeta basis set which contains two functions for each nl shell occupied in the separated atoms (Schaefer 1974; Pople 1973). Reliable predictions of one-electron operator properties, such as the electric dipole moment and field gradient, on the other hand, require near HF basis sets.

To obtain the equilibrium geometry of N_2H^+ we have calculated the SCF energy as a function of $r(\text{NN})$ and

$r(\text{NH})$, the nitrogen-nitrogen and nitrogen-hydrogen bond lengths, using a double-zeta basis set, and assuming that N_2H^+ , like HCN, is linear. The minimum energy is found when $r(\text{NN}) = 1.099 \text{ \AA}$ and $r(\text{NH}) = 1.041 \text{ \AA}$. Similar calculations on other molecules indicate that these values are probably accurate to about 1 percent. The rotation constant is then calculated to be $B_e = 46.3 \pm 0.9 \text{ GHz}$, and the frequency of the $J = 1 \rightarrow 0$ rotational transition to be $\nu_{10} = 2B_0 = 2B_e - \alpha_1 - 2\alpha_2 - \alpha_3 = 92.2 \pm 1.8 \text{ GHz}$, where for the rotation-vibration constants it has been assumed that as in HCN, $\alpha_1 + 2\alpha_2 + \alpha_3 \simeq 0.4 \text{ GHz}$.

To obtain the electric field gradients at the two nitrogen nuclei and the permanent electric dipole moment of N_2H^+ , we have computed a large-basis, near-HF wave function at the calculated equilibrium geometry. Taking $Q_N = 1.56 \times 10^{-26} \text{ cm}^2$ (O'Konski and Ha 1968) for the nitrogen quadrupole moment, the quadrupole coupling constants for the outer and inner nitrogens are calculated to be $-5.3 \pm 0.5 \text{ MHz}$ and $-1.2 \pm 0.5 \text{ MHz}$, respectively. The electric dipole moment (with respect to the center of mass) is calculated to be $\mu = 3.4 \pm 0.5$ debye. The quoted uncertainties are estimates based on similar calculations on molecules for which experimental data is available (see, e. g., Green 1974).

Figure 1 shows the hfs of the $J = 1 \rightarrow 0$ transition of N_2H^+ calculated from the SCF quadrupole coupling constants. At the narrowest line widths observed by Turner, about 1.2 MHz, the predicted structure due to the inner nitrogen is indeed seen to be entirely unresolved. Resolving it in very narrow-line sources though is not out of the question, and it is clear that this would provide strong support for the assignment.

Although much more costly and time-consuming than the SCF calculations described here, configuration interaction (CI) calculations should significantly improve the reliability of these predicted properties. For example, rotation constants can be predicted to better than 0.5 percent accuracy from CI calculations (see, e.g., Schaefer 1974; Pearson *et al.* 1973). Furthermore, the uncertainty in the dipole moment could be reduced to 0.1 debye and, more importantly, the uncertainties in the quadrupole coupling constants could be reduced to 0.2 MHz. CI calculations for N_2H^+ are currently under way in this laboratory.

Finally we note that the identification of N_2H^+ is reasonable in terms of current ideas of interstellar chemistry. A large fraction of the available carbon and oxygen is found to exist as the very stable CO molecule, with only trace amounts of these elements in all the other molecules observed. Much of the available nitrogen is similarly expected to exist as N_2 , which is iso-electronic with CO and equally stable, but which of course cannot be observed at radio frequencies. Observations of other nitrogen-containing species have accounted for only a tiny fraction of the nitrogen expected in interstellar clouds. As noted by Herbst and Klemperer (1973), fast ion-molecule reactions are probably important in interstellar chemistry. Such reactions with the very abundant CO molecules should lead to appreci-

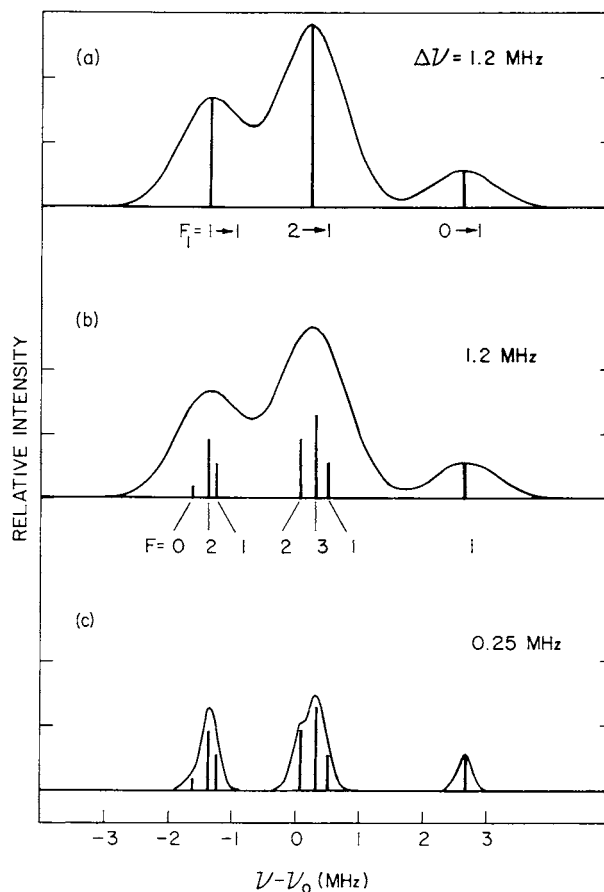


FIG. 1.—Predicted hfs of the $J = 1 \rightarrow 0$ transition of N_2H^+ . (a) The hfs expected from only the outer nitrogen. In (b) the hfs of the inner N is included. It is seen to have a negligible effect on the observed structure when the line width (full width at half-maximum) is 1.2 MHz, which is about the smallest observed by Turner. However, in (c) the effects of the inner N begin to emerge when $\Delta\nu \approx 0.25 \text{ MHz}$. Broadening of the central $F_1 = 2 \rightarrow 1$ line, with a consequent reduction of its peak intensity, is probably the most easily observed effect.

able amounts of the molecular ion HCO^+ , which Klemperer (1970) has suggested is the carrier of the “X-ogen” interstellar line at 89.1 GHz. Because N_2 is expected to be nearly as abundant as CO in interstellar clouds, and because N_2 and CO are analogous chemically, reactions similar to those which lead to HCO^+ are also expected to produce N_2H^+ . The identification of N_2H^+ therefore supports in a general way the identification of X-ogen with HCO^+ .

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